LATENT HEAT AND CRYSTALLIZATION OF FATTY ACIDS

Some Practical Considerations in Preparation of Mixed Fatty Acids of Tallow for Pressing.

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Abstract

Methods and procedure in preparing mixed fatty acids of tallow for pressing to obtain oleic acid are generally discussed. Experimental determinations of the specific heat and latent heat thermal capacities are described. Upon the basis of these determinations the required mechanical refrigeration capacity is estimated. Applicable types of refrigeration equipment are discussed and compared.

THE production of stearic and oleic acid from the mixed fatty acids of tallow by means of crystallization and pressing is a well known art, probably nearly as old as the commercial production of candles. The procedure which has been in most general use for many years comprises crystallizing the mixed fatty acids by slow chilling in pans and pressing the cakes thus formed in hydraulic presses.

In this operation the bulk of the oleic acid (red oil) flows from the presses, leaving in the press cloths a mixture of stearic acid with some red oil, which mixture is recrystallized and again pressed in steam-heated presses for production of stearic acid. It is well-known, of course, that the "stearic" acid of commerce, produced from tallow and similar fats, is in reality a mixture of stearic and palmitic acids.

Only the primary crystallization, prior to the first pressing operation, will be dealt with herein.

Lewkowitsch[3] reports the melting point of the mixed fatty acids of tallow as 43.0° C. to 44.0° C. (109.4° F. to 111.2° F.) and the solidifying point (titer test) as 43.5° C. to 45.0° C. (110.3° to 113.0° F.).

The same author[4] reports the melting point of oleic acid as 6.5° C. (43.7° F.), the solifying point as 4.0° C. (39.2° F.). For palmitic acid the figures are: melting point 62.6° C. (144.7° F.) solidifying point the same, and for stearic acid: melting point 69.3° C. (156.75° F.), solidifying point the same. It should be noted that there has been considerable controversy concerning the melting point of oleic acid, vari-

[1]Century Stearic Acid Candle Works, Inc.
[2]Alan Porter Lee, Inc.
[3]Chemical Technology and Analysis of Oils, Fats and Waxes, 6th Ed., Vol. II, p. 779.
[4]Ibid., Vol. I, pp. 183, 162, 166.

ous observers having reported values from 6° C to 16° C.

The figures given for melting and solidifying points of the mixed fatty acids of tallow indicate the effect of mixtures upon the constants for the individual acids. A generally accepted average composition of mixed tallow fatty acids is:

Oleic acid 45%
Stearic acid 23%
Palmitic acid 32%

The first pressing problem becomes, then, one of recovering as much as possible of the 45 per cent of contained oleic acid in a state of complete or nearly complete freedom of admixed palmitic or stearic acid.

Commercial practice in stearic acid plants in this country has generally involved cooling the fatty acid mixture in pans containing approximately 14 lbs. each. The pans are constructed of aluminum or other non-corrosive metal and are usually tiered in racks and filled by cascading from a supply trough placed above each rack.

After cooling and crystallization of the fatty acids, the cakes are emptied from the pans to press-cloths and pressed in hydraulic presses at from 150 to 250 pounds per square inch.

The figures given above for melting and solidifying points of the mixed acids and of the pure oleic acid furnish a key to the technic of cooling which must be employed to obtain satisfactory results in pressing.

In order to have suitable crystallization of the saturated acids in the magma of oleic acid, the chilling must progress slowly and the entire mass of mixed acids must be charged to the cooling pans at a temperature well above that at which crystallization will begin, in order that there shall be no crystal formation before the mixture is resting quietly in the pans.

The purpose of this is to promote the formation of complete well-built crystals and avoid damage to the crystals by motion while the mixture is flowing to the pans.

Experience has shown that a suitable temperature range for filling the pans is from 130° F. to 140° F., in order that the temperature of the

mixed acids shall not be lower than 115° F., when all pans in a rack are finally filled by cascading.

Cooling must proceed at a reasonably slow rate from 115° F. to 40°-48° F. (maximum 50° F.), when the crystallized mixture of acids will be ready for transfer to the press cloths, thence to the presses.

During the winter season, such cooling is effected easily through the use of atmospheric temperatures, without resort to any mechanical refrigeration, but in the climatic zones of this country, artificial cooling aid is imperative for conduct of the operation in summer, if it is desired to produce low titer red oil—that is, practically pure oleic acid.

Recent research in connection with design of suitable mechanical refrigeration for summer use in a commercial plant producing oleic acid has developed some interesting data relative to the crystallizing characteristics of these mixed fatty acids and the amount of refrigeration necessary to produce the desired degree of cooling.

As is well known, the total heat to be removed includes specific heat and latent heat of crystallization, or change of state. In order to evaluate the amounts of these two types of heat to be removed, arrangements were made to obtain accurate measurements of the specific and latent heat capacities involved.

The determinations were performed by a leading physical testing laboratory, in a vacuum calorimeter, according to the method of Southard and Brickwedde,[5] which involves careful electrical measurement of the amount of heat input necessary to raise the temperature of one pound of the mixed fatty acids through each of a series of small temperature increments between 40° F. and 170° F.

The pot of the calorimeter used was heavily gold-plated for avoidance of corrosion by the fatty acids, the heat input being measured in terms of electric energy by means of an accurate wattmeter.

Suitable precautions were taken to prevent radiation and convection losses, and temperature readings were taken by means of thermo-

[5]J. A. C. S., Vol. LV, p. 4378, 1933.

couples and a copper resistance thermometer.

The pot, capable of holding about 1 lb. of the sample, was provided with a central tube containing a 100-ohm heater coil and a 100-ohm copper resistance coil wound concentrically on a brass tube.

With its sample, heater and thermometer, the pot was set on an insulating support in an enclosing covered can which was wrapped with a heater coil. The pot-and-can assembly was placed in a silver-plated glass Dewar flask provided with an air-tight "Bakelite" cover to which were attached terminals for the electric connections and a vacuum-hose coupling. The Dewar flask was mounted in a metal sheath heavily insulated with felt.

The flask having been evacuated, heat was supplied to the can heater until thermocouples attached to the can and to the pot showed both to be at the same temperature within a few hundredths of a degree Fahrenheit. Sufficient readings of the resistance of the copper thermometer were then taken to be sure that thermal stability had been reached.

A measured quantity of electrical energy was then supplied to the pot heater, followed by an hour's observation of temperature rise.

After a condition of thermal stability was reached, a second measured quantity of energy was supplied to the pot and the procedure above repeated. In this manner, by successive steps the entire desired temperature range was covered.

During the period of the tests, temperature of the can was maintained continuously at the temperature of the pot (within a fraction of a Fahrenheit degree) by judicious application of electrical energy to the can heater.

The pot being thus surrounded by metal surfaces at its own temperature, radiation and convection losses from it were eliminated. Conduction losses through the fine copper wire electrical leads were negligible.

The heat content of the apparatus alone was determined in a separate run and the accuracy of the method was demonstrated by still another run, in which the specific heat values obtained for water agreed with accepted values within 1 per cent.

Thompson and Koenig[6] report the findings of the experimental work as follows:

"The mass of the specimen (of mixed fatty acids) used for the measurement was 1.003 lb. The calorimeter and its contents were cooled below 40° F. before beginning the series of measurements. Small increments of heat were required to cover the desired temperature range from 40° F. to 170° F.

"The following table shows the average temperature of each of the 20 runs, the heat absorbed by the mixed fatty acids and the corresponding rise in temperature. The effective thermal capacity was computed from these quantities.

TABLE I.

Run No.	Temp., Mean	Fahr. Rise	Heat, B.t.u. per lb. For Run	Per deg. Fahr.*
1....	42.8	9.30	5.55	0.595
2....	54.0	8.98	5.66	0.63
3....	63.3	8.24	5.87	0.715
4....	72.2	7.36	6.15	0.835
5....	78.3	7.40	6.13	0.83
6....	84.3	6.60	6.39	0.97
7....	89.3	6.48	6.43	0.99
8....	93.6	6.39	6.46	1.01
9....	95.1	3.14	3.25	1.035
10....	98.4	4.47	7.08	1.585
11....	102.0	3.85	7.24	1.88
12....	104.8	3.14	7.51	2.39
13....	107.3	3.30	7.46	2.26
14....	111.5	8.13	5.86	0.72
15....	113.0	4.79	2.69	0.56
16....	119.5	10.03	5.22	0.52
17....	128.1	9.64	5.35	0.555
18....	138.5	14.22	8.08	0.57
19....	150.8	14.08	8.12	0.575
20....	163.1	14.08	8.10	0.575

*i. e., effective thermal capacity.

[6]Electrical Testing Laboratories unpublished report. (Quoted with permission.)

"Table II, below shows the heat absorbed by 1 lb. of the mixed fatty acids is assumed to have an average value of 0.56 B.T.U. per lb. over the temperature range 40° F. to 170° F., then the heat absorbed in change-of-state (fusion) will appear as shown in Table II.

From these figures it is evident that cooling such mixed fatty acids from 130° to 40° will require removal of 50.4 B.T.U. per lb. of specific heat and 30.1 B.T.U. per lb. of latent heat, a total of 80.5 B.T.U. per lb.

In practice it has been considered convenient to perform the first cooling (from 130° to 100°) without the aid of refrigeration, as this can be accomplished through the medium of uncooled air even in the summer months.

A recent installation was planned to cool 30,000 lbs. of mixed fatty acids from pan-filling temperature (130° F.) to 40° F. in a total of 16 hours, devoting eight hours to cooling with atmospheric air from 130° F. to 100° F. and the remaining eight hours to cooling with the aid of mechanical refrigeration from 100° F. to 40° F. From Table II below it is evident that in the pre-

"TABLE II.

Temp. Range, Fahr.	Total	Heat Absorbed, B.t.u. per lb. Specific Heat "Thermal Capacity"	Latent Heat "Change-of-State"
40°- 70°	19.7	16.8	2.9
70°-100°	30.1	16.8	13.3
100°-130°	30.7	16.8	13.9
130°-170°	22.95	22.4	0.55
Total	103.45	72.8	30.65."

acids when the temperature is raised by the intervals shown, as computed from the experimental results. If the 'true thermal capacity' (that is, the specific heat) of the mixed fatty liminary cooling it is necessary to remove 16.8 B.T.U. per lb. of specific heat and 13.9 B.T.U. per lb. of latent heat, a total of 30.7 B.T.U. per lb. in eight hours, for
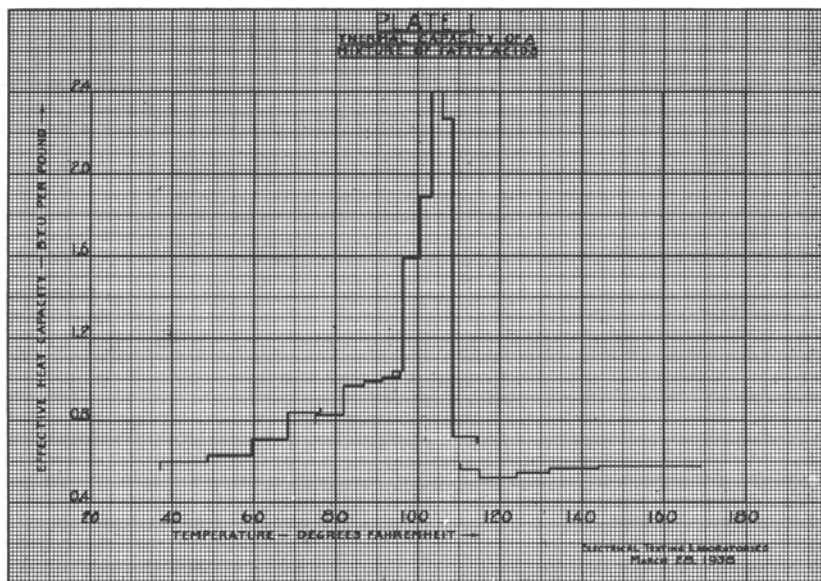
an average of 3.84 B.T.U. per lb. per hour.

This will leave a remainder of 33.6 B.T.U. of specific heat and 16.2 B.T.U. of latent heat, totaling 49.8 B.T.U. per lb. to be removed in 8 hours with the aid of mechanical refrigeration.

The chart shown in *Plate I,* presents a graphic representation of the measured flow of heat from the fatty acid mixture during cooling. The experimental determinations were made by heating previously cooled material, but it will be conceded that the line of exothermy during cooling will be identical with that of the endothermic effect during heating.

It will be noted from the chart that crystallization occurs initially just below 115° F. and proceeds most rapidly between 108° and 82° F.

From this point to 40° F. crystallization is slow but small in quantity, being for all practical purposes complete at 49° F.

In order to determine the amount of refrigeration required for the cooling from 100° to 40° F. in eight hours it was decided to assume that the fall in *temperature* would be uniform throughout the eight hours, that is, at the rate of 7.5° per hour.

Upon this assumption, Table III is prepared, using the average specific heat of 0.56 B.T.U. per lb. and latent heats read from the chart for the different temperature ranges of the several hours.

Referring to the chart (Plate I), it will be seen that between the temperatures of 100° F. and 97° F. there is a total heat release of 1.6 B.T.U. per pound per degree, or 4.8 B.T.U. per pound, of which 1.68 B.T.U. represents specific heat at 0.56 per pound per degree, the remaining 3.12 B.T.U. per pound consisting of latent heat. Similarly, between 97° and 92.5° there is released 4.58 B.T.U. per pound consisting of 2.52 B.T.U. specific and 2.06 B.T.U. latent heat, each per pound. This shows a total of 4.2 B.T.U. specific heat + 5.18 B.T.U. latent heat = 9.38 B.T.U. per pound total heat to be removed during the first hour.

For 30,000 lbs. this equals 281,400 B.T.U. or 0.98 tons of refrigeration in one hour, equivalent to 23.5 tons refrigeration capacity in 24 hours, without allowance for chilling of pans and racks, or for radiation losses.

Similarly to cool from 92.5° F. to 85° F. there is required removal

of 4.2 B.T.U. specific heat + 3.22 B.T.U. latent heat per pound × 30,-000 = 222,600 B.T.U. = 0.88 ton refrigeration, equivalent to 21.1 ton daily refrigeration machine capacity.

In like manner the load can be calculated for each hour assuming 7.5° temperature reduction per hour producing the following table.

TABLE III.

Refrigeration Load Required to Cool 30,000 lbs., Mixed Fatty Acids from 100° to 40° F. at Rate of 7.5° per hour. (No allowance for Pan Cooling or Radiation Losses.)

Hr.	Temp. Range	Sp. Ht. B.t.u. per lb.	Latent Ht. B.t.u. per lb.	Total B.t.u.	Tons Refrig. Actual	Rate per Day
1	100.0–92.5°	4.2	5.18	231,400	0.98	23.5
2	92.5–85.0°	4.2	3.22	222,600	0.77	18.5
3	85.0–77.5°	4.2	2.52	201,600	0.70	16.8
4	77.5–70.0°	4.2	2.01	186,300	0.65	15.6
5	70.0–62.5°	4.2	1.405	168,150	0.59	14.2
6	62.5–55.0°	4.2	0.905	153,150	0.53	12.8
7	55.0–47.5°	4.2	0.66	145,800	0.51	12.3
8	47.5–40.0°	4.2	0.30	135,000	0.47	11.3
Totals	100°–40°	33.6	16.20	1,494,000	5.20	15.6

These figures indicate a total demand of 5.2 tons of refrigeration per eight hours or 15.6 tons per 24 hours with a maximum hourly demand at the rate of 23.5 tons per day.

For the cooling of 30,000 lbs. of fatty acids there will be required 2,143 aluminum pans, each holding 14 lbs. of acid mixture and each pan weighing 2 lbs.

There must be cooled, therefore, 4,286 lbs. of aluminum, with specific heat of approximately 0.3, from 100° to 40° F. This will require removal of 18 × 4,286 = 77,148 B.T.U. in 8 hours, equivalent to 0.27 tons of refrigeration in that period or 0.8 ton per day.

In similar manner the thermal capacity of the pan racks can be established as not exceeding 0.5 ton of refrigeration daily.

Another factor to receive consideration must be radiation loss through the walls of the chilling room. The amount of this will vary in accordance with each of several factors, being affected particularly by the type and amount of insulation used in construction of the chill room, by the mean temperature difference between the outside and inside air and by velocity of the inner air past the insulated surfaces in

cases where cooling is accomplished by methods embracing air circulation.

It is outside the scope of this brief discussion to take up the mathematical formulae involved in estimation of the amount of refrigeration required to compensate for radiation losses and it will suffice here to say that for a plant of the size above outlined an allowance of 2.5 tons of refrigeration for this purpose has been considered ample.

The refrigeration machine capacity required can then be tabulated as follows:

TABLE IV.

Refrigeration Machine Capacity Required for Crystallizing 30,000 lbs., Mixed Fatty Acids in Pans from 100° to 40° F. in 8 hours.

	Required for	Actual Consumption per 8 hrs.	Actual Consumption per 24 hrs.	Maximum Hourly Demand	Mach. Rate per 24 hrs. based on Max. Demand
1.	Chilling Acids	5.20	15.60	0.98	23.5
2.	Chilling Pans and Racks	0.43	1.29	0.06	1.4
3.	Replacing Radiation Losses	0.80	2.40	0.10	2.5
	Totals	6.43	19.29	1.14	27.4

The figures of Table IV indicate that for proper handling of the task outlined 27.4 tons of refrigeration machine capacity is required, but that it possibly may be done with a slightly smaller machine by permitting hourly variations in the rate of temperature drop in the acids, that is, accepting a rate of less than 7.5° F. per hour when the bulk of the latent heat is being removed and compensating for this reduction in rate by acceleration in hourly rate (above 7.5° F. per hour) after the bulk of the latent heat of crystallization has been dissipated.

It is considered that such an endeavor to keep refrigeration machine size at a minimum would be unwise and that the machine should be installed of ample size to handle the peak load.

In choosing mechanical refrigeration for a task of the type herein described, the operator may select one of several types of equipment, the most popular being ammonia

compression, freon compression and steam-jet vacuum.

Since the major portion of the work must be done at relatively high temperatures, the freon compressor would seem to be preferable to the ammonia machine, because of the greater efficiency of the former at high temperatures.

The steam-jet-vacuum equipment, in cases where steam is relatively less costly than other forms of power, offers attractions in that it does not require any chemical other than water and is extremely efficient at moderately high temperatures.

When the type of refrigeration machine to be used has been selected it is necessary to determine the means of application of refrigeration to the cooling room and thus to the fatty acids in the pans.

With the freon machine, direct expansion coils may be used in the chilling room, or with the steam-jet machine, the refrigerating medium, water, may be pumped through similar coils in the room.

Modern tendency, however, is toward positive circulation of the air in the cooling room, which calls for adoption of air-conditioning

methods, generally involving a bunker room containing the direct-expansion or cooling-water coils; a fan to develop positive air circulation through a system of insulated ducts leading to the cooling room and returning to the bunker room. Such a system can be equipped for positive circulation of air from outdoors during the winter season.

The design of this type of air-circulating system involves many problems, including selection of the proper volume and velocity of air, proper design of distributing system to insure contacting of all the pans by the cold air, suitable sizing of the refrigeration coils, the fan and the ducts, proper insulating of the ducts and correct proportioning of the return ducts to those used for cold air in order to avoid building excessive atmospheric pressure in the chilling room.

The correct mean temperature differences between the cooling air and the fatty acids and between the return air and the refrigerant coils are of utmost importance.

Freon and cold water here demonstrate their superiority over ammonia as refrigerant mediums in

that they can be handled at higher temperatures in the cooling coils and are thus less likely to cause icing of the coils from precipitation of moisture from the circulating air.

In general terms, moving a relatively large volume of air at low velocity through a duct system so designed as to insure maximum contact of the air with the fatty acids in the pans and returning the air over refrigerant coils of large surface in which the refrigerant medium flows at temperature high enough to avoid excessive frosting or icing, will result in efficient solution of the problems involved. In some instances it may be necessary or desirable to interpose some type of air dryer such as one utilizing activated alumina, in the return ducts between the cooling room and the refrigerant coils.

In the light of modern progress of air-conditioning design those engineers specializing in this art are able to reduce to positive mathematical formulae all of the factors inherent in the design of such chilling equipment as has been herein discussed.

REPORT OF SOAP STOCK COMMITTEE
AMERICAN OIL CHEMISTS' SOCIETY 1937-38

THE work of the Soap Stock Committee has been confined to a study of the official and optional official methods for the determination of total fatty acids in acidulated and non-acidulated soap stock. In order to compare the results given by the two methods, identical samples of acidulated soap stock were analyzed by the members of the committee (Table I).

TABLE I
Acidulated Soya Bean and Corn Oil Soap Stock (Sample 1).

	Official Method % T.F.A.	Optional Official or Wet Extraction Method % T.F.A.
Barrow	94.17	93.84
Lappen	90.33	94.31
Long	94.12	93.82
Reese	93.45	*91.79
Rich	95.09	94.78
Watkins	93.66	92.09
Average	93.47	93.44
High	95.09	94.78
Low	90.33	91.79

*1-125 cc. and 5-25 cc. extractions. 2-100 cc. and 2-50 cc. extractions 92.93% T.F.A.

Next, using the official method, experiments were conducted in which the fatty acid cake was dried at room temperature and at 50-55° F. With the optional official, or wet extraction method, the fatty acids were extracted with warm

petroleum ether, varying quantities of solvent, and the solvent held in contact with the fatty acids over night. Tests were also made in which the fatty acids were dried at 100° C. and 105° C. The results of these tests are given in Table II. Two samples of acidulated corn oil soap stock were analyzed by several members of the committee using some of these modifications (Table III).

The data in Table II and III indicate that either method as now written gives satisfactory results. However, it appears that definite improvement can be made by rewriting both methods, making the directions more specific and consistent. Drafts of the methods containing these modifications were submitted to the committee. Additional improvements were suggested and incorporated.

In order to determine the effect of different amounts of solvent in the proposed wet extraction method, tests were made on two samples of acidulated soap stock using varying quantities of petroleum ether. These samples were also

analyzed by the proposed dry extraction method (Table IV). Tests were made to determine the minimum number of extractions required in the wet extraction method (Table V).

Making only minor changes in the proposed methods a total of nine samples of soap stock and seven of acidulated soap stock were analyzed. In order to obtain as much data as possible, the work was divided so as to have most of the samples analyzed by three or four members. The results of the tests are given in Table VI, and summarized in Table VII.

The methods which were approved by the committee are as follows:

PROPOSED DRY EXTRACTION METHOD FOR TOTAL FATTY ACIDS OF ALL SOAP STOCK AND ACIDULATED SOAP STOCK, EXCEPT FROM COPRA AND PALM KERNEL OILS

Weigh out from a weighing bottle 8 to 10 grams of a well mixed sample of soap stock or 4 to 5 grams of acidulated soap stock and transfer to a 400 cc. beaker. Sa-